Mössbauer Spectra of Organotin Compounds. Part IV.[1] Compounds Containing Sn–S Bonds [2]

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It is shown that Mössbauer spectroscopy can be used to assign configurations to adducts of tetrathiolatotin compounds of the type SnX_4Y_2 (X = S, Y = N or O). The signs of the electric field gradients are +ve for a *cis*- and −ve for a *trans*-isomer. Some new triphenyltin and tributyltin thiolates and thioacetates have been prepared; the Mössbauer spectra of these and other compounds are reported and discussed.

ALTHOUGH Mössbauer parameters have been recorded for a large number of organotin compounds, relatively few reports have been made on compounds containing Sn–S bonds.[3-5] Here we report Mössbauer parameters for two types of thiolatotin compounds and interpret the results in terms of the structures of the compounds.

TABLE 1

Mössbauer parameters for tetrathiolatotin compounds [a]

Compound number	Compound	δ	Δ	Γ_1	Γ_2	R [b]
(1)	$\mathrm{Sn(edt)_2}$ [c]	1·44	1·07	0·90	0·92	0·12
(2)	$\mathrm{Sn(p2dt)_3}$	1·43	0·96	0·81	0·84	0·056
(3)	$\mathrm{Sn(p3dt)_2}$	1·38	0·0	0·93		0·054
(4)	$\mathrm{Sn(tdt)_2}$	1·21 [d]	1·52 [d]			0·40 [d]
(5)	$\mathrm{Sn(SPh)_4}$	1·47	0·0	0·82		0·0

[a] Abbreviations: edt = ethane-1,2-dithiolato. p2dt = Propane-1,2-dithiolato. p3dt = Propane-1,3-dithiolato. tdt = Toluene-3,4-dithiolato. [b] R = The ratio of the Mössbauer effect at room temperature to that at 78 K. [c] Epstein and Straub (ref. 6) reported δ = 1·34, Δ = 0·98 mm s^{-1}. [d] Results taken from ref. 6.

Compounds Containing Four Sn–S *Bonds*.—The results of Mössbauer studies on some spirocyclic bis(dithiolato)tin compounds and on tetraphenylthiolatotin are given in Table 1. The large Mössbauer effect at room temperature shown by compound (4) [6] supports the view that this compound has a polymeric structure with six-coordinate tin atoms.[7] Although compound (1) is monomeric in solution [7] simple monomeric tetrahedral structures are ruled out for compounds (1)—(3) in the solid state by the significant [1] room-temperature effects and also, for compounds (1) and (2), by the presence of a quadrupole interaction. It seems likely that compounds (1)—(3) are weakly associated, though the principal cause of distortion of the tetrahedral configuration appears to be related to the presence of the somewhat strained five-membered ring systems in compounds (1) and (2). The structural significance of the remarkably low solubility of compound (3) is uncertain.[7] The absence of both a quadrupole splitting and a room-temperature effect for tetraphenylthiolatotin is consistent with a simple tetrahedral structure and the isomer shift should be compared with those of tin(IV) iodide (1·45 mm s^{-1}) [8] and tetramethyltin (1·29 mm s^{-1}).[9]

Compounds (1)—(5) form adducts with mono- and bi-dentate donor molecules and Mössbauer parameters for this class of compound are presented in Table 2.

TABLE 2

Mössbauer parameters and configurations of adducts of tetrathiolatotin compounds [a]

Compd. no.	Compound	δ	Δ	Γ_1	Γ_2	Configuration
(6)	$\mathrm{Sn(edt)_2}$(2,2′-bipyridyl)	1·06	1·17	0·81	0·88	*cis*
(7)	$\mathrm{Sn(edt)_2}$(1,10-phenanthroline) [b]	1·03	1·06	0·85	0·85	*cis*
(8)	$\mathrm{Sn(edt)_2}$(2,2′-bipyridylamine)	1·09	1·26	0·83	0·87	*cis*
(9)	$\mathrm{Sn(edt)_2,(pyridine)_2}$ [b]	1·06	1·86	0·81	0·90	*trans*
(10)	$\mathrm{Sn(edt)_2}$,(4-methylpyridine)$_2$	0·99	1·88	0·75	0·77	*trans*
(11)	$\mathrm{Sn(edt)_2,(Et_2SO)_2}$	1·04	1·94	0·75	0·85	*trans*
(12)	$\mathrm{Sn(edt)_2,(Me_3NO)_2}$	0·62	1·15	0·77	0·89	*cis*
(13)	$\mathrm{Sn(p3dt)_2}$(2,2′-bipyridyl)	1·07	1·02	0·83	0·83	*cis*
(14)	$\mathrm{Sn(p3dt)_2}$(1,10-phenanthroline)	1·07	0·87	0·85	0·85	*cis*
(15)	$\mathrm{Sn(p3dt)_2,(pyridine)_2}$	1·08	1·77	0·81	0·85	*trans*
(16)	$\mathrm{Sn(p3dt)_2}$,4-methylpyridine)$_2$	1·07	1·79	0·73	0·85	*trans*
(17)	$\mathrm{Sn(p2dt)_2}$(2,2′-bipyridyl)	1·06	1·08	0·80	0·85	*cis*
(18)	$\mathrm{Sn(p2dt)_2}$(1,10-phenanthroline)	1·08	1·17	0·78	0·85	*cis*
(19)	$\mathrm{Sn(p2dt)_2,(Et_2SO)_2}$	1·07	1·95	0·85	0·88	*trans*
(20)	$\mathrm{Sn(p2dt)_2}$,(4-aminopyridine)$_2$	0·99	1·38	0·84	0·90	*cis?*
(21)	$\mathrm{Sn(SPh)_4}$(2,2′-bipyridyl)	1·14	0·81	0·74	0·85	*cis*

[a] Abbreviations: edt = ethane-1,2-dithiolato. p2dt = Propane-1,2-dithiolato. p3dt = Propane-1,3-dithiolato. [b] Previously reported (ref. 6) values: compound (7) δ = 0·96, Δ = 1·00; compound (9) δ = 1·05, Δ = 1·84 mm s^{-1}.

A previous analysis of the i.r. spectra of adducts of bis(ethane-1,2-dithiolato)tin showed that, generally, monodentate ligands gave *trans*-adducts but trimethylamine oxide was exceptional in giving a *cis*-complex.[10] It was predicted from point-charge calculations that, for complexes of the type SnX_4Y_2, the magnitude of the quadrupole splitting for the *trans*-isomer should be

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[7] R. C. Poller and J. A. Spillman, *J. Chem. Soc.* (*A*), 1966, 958.

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approximately twice that of the corresponding *cis*-compound.[11] Although this prediction was shown to be correct for organotin complexes of the type R_2SnX_4 it has not hitherto been tested with other classes of SnX_4Y_2 compounds. Examination of Table 2 shows that the *cis*-adducts of bis(ethane-1,2-dithiolato)tin (compounds 6, 7, 8, 12) have quadrupole splittings of *ca.* 1 whereas the *trans*-compounds (9)—(11) have values of *ca.* 2 mm s^{-1}. The relationship $\Delta(trans) \simeq 2\Delta(cis)$ is therefore valid and this is confirmed by the fact that compounds (13), (14), (17), (18), and (21) which are derived from chelating ligands and hence have *cis*-configurations also have $\Delta = ca.$ 1 mm s^{-1}. *trans*-Configurations are therefore assigned to compounds (15), (16), and (19) which have quadrupole splittings of *ca.* 2 mm s^{-1}. The configuration of compound (20) must be regarded as tentative since the Δ value is higher than those of the other *cis*-compounds. This intermediate value of the quadrupole splitting indicates molecular distortion, but the structure may be complicated by the presence of the two nitrogen atoms in the ligand. We are unable to account for the fact that in previous work [7] a 1 : 1 adduct was isolated from treatment of bis(propane-1,3-dithiolato)tin with pyridine whereas the Mössbauer parameters of the product (compound 15) obtained in the present work indicate that it is a 2 : 1 adduct [*cf.* compound (16)].

For SnX_4Y_2 compounds in which Y = C and X is an atom which is more electronegative than carbon, the predicted signs of the quadrupole splittings are *trans*+ and *cis*−, though due to distorted geometries this sign reversal has not been observed.[12] In the present SnX_4Y_2 compounds X = S and Y = N or O and the electronegativities are Y > X, the predicted signs of the quadrupole splitting are *trans* negative and *cis* positive. Mössbauer measurements of the bipyridyl and diethyl sulphoxide adducts of bis(ethane-1,2-dithiolato)tin [compounds (6) and (11)] in a 60 kG magnetic field gave well resolved spectra (Figures 1 and 2) from which it was shown by a computer-fitting procedure that the sign of e^2qQ for the *cis*-compound (6) is positive and that for the *trans*-compound (11) is negative. This confirms the assigned geometries for these compounds but, more importantly, it is the first example of electric field gradient sign reversal in *cis*- and *trans*-octahedral complexes.

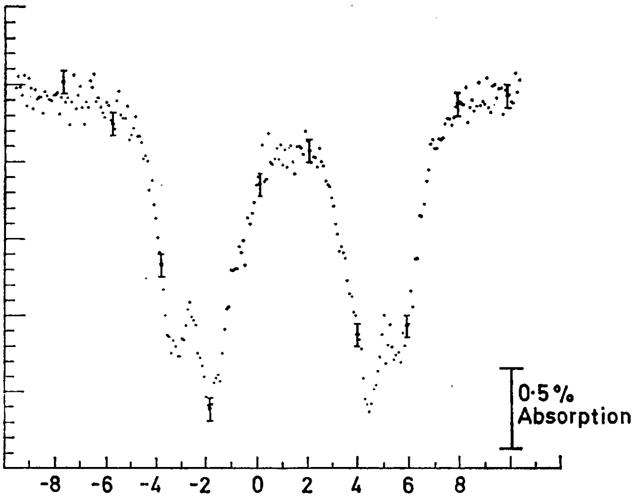

FIGURE 1 Spectrum of $Sn(edt)_2,(2,2'\text{-bipyridyl})$ (compound 6) at 4 K in a magnetic field of 60 kG

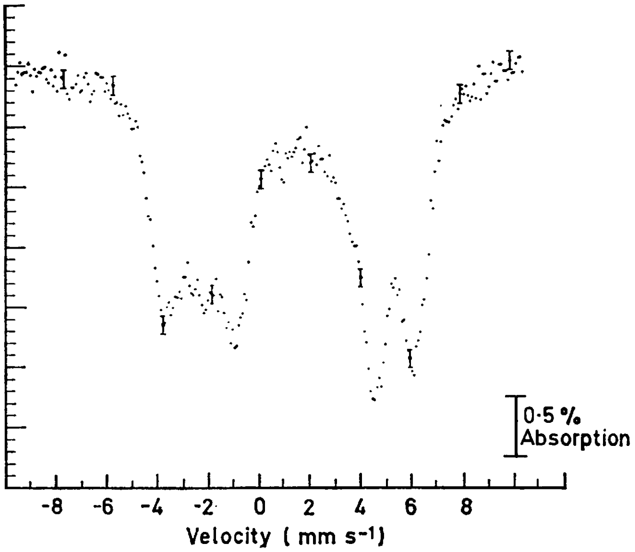

FIGURE 2 Spectrum of $Sn(edt)_2,(Et_2SO)_2$ (compound 11) at 4 K in a magnetic field of 60 kG

The isomer shifts of the adducts shown in Table 2, with the exception of compound (12), are remarkably consistent showing a variation of only $\pm 0{\cdot}1$ mm s^{-1}. These values are about 0·3 mm s^{-1} lower than those of the parent compounds reflecting use of the 5*d* orbitals on adduct formation. This increased *d*-electron density around the tin atom leads to a greater shielding of the *s* electrons and hence a lowered isomer shift. The reason for the low value of the isomer shift shown by the trimethylamine oxide adduct of bis(ethane-1,2-dithiolato)tin is not clear though this compound is also exceptional amongst the adducts derived from monodentate ligands in having the lowest quadrupole splitting.

The isomer shifts of the four 2,2′-bipyridyl derivatives in Table 2 (compounds 6, 13, 17, and 21) are very similar, the mean value being 1·08 mm s^{-1}. When the isomer shifts of the corresponding adducts of the tin tetrahalides [13] SnX_4,2,2′-bipyridyl (X = Cl, Br, or I) are plotted against the (Pauling) electronegativities of X a straight line is obtained. Using this linear relationship a value of 2·56 is obtained for the electronegativity

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of sulphur, in good agreement with the literature[14] value of 2·58.

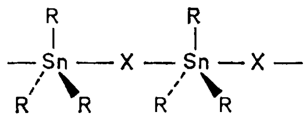
TABLE 3

Mössbauer parameters of monothiolatotin compounds

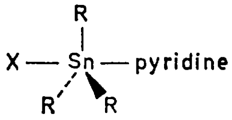
Compd. no.	Compound	Phase[a]	δ	Δ	Γ_1	Γ_2
(22)	$Bu_3Sn{\cdot}SAc$	S	1·43	2·40	0·82	0·81
		P	1·44	2·87	0·77	0·80
(23)	$Bu_3Sn{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}$-$SnBu_3$	S	1·39	1·75	0·80	0·81
		P	1·37	2·02	0·75	0·88
(24)	$Bu_3Sn{\cdot}SPh$	S	1·42	2·03	0·88	0·82
		P	1·43	2·62	0·87	0·88
(25)	$Bu_3Sn{\cdot}S{\cdot}C_6H_4{\cdot}NH_2$-2	S	1·43	1·99	0·91	0·92
		P	1·43	2·67	0·88	0·91
(26)	$Ph_3Sn{\cdot}SAc$	S	1·31	1·65	0·82	0·85
		P	1·34	2·35	1·05	1·08
(27)	$Ph_3Sn{\cdot}SPh$[b]	S	1·32	1·41	0·84	0·87
		P	1·38	2·39	0·85	0·85
(28)	$Ph_3Sn{\cdot}S{\cdot}C_6H_4{\cdot}NH_2$-2	S	1·33	1·55	0·77	0·86
		P	1·28	2·15	0·85	0·90
(29)	$Ph_3Sn{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}$-$SnPh_3$	S	1·32	1·22	0·81	0·79
		P	1·30	1·25	0·90	0·95
(30)	$Ph_3Sn{\cdot}S{\cdot}C_5H_4N$-2[c]	S	1·36	1·58		
		P	1·45	1·72		
(31)	$Ph_3Sn{\cdot}S{\cdot}C_5H_4N$-4[c]	S	1·37	2·61		
		P	1·36	2·54		

[a] S = Solid; P = frozen pyridine solution. [b] Literature values (solid state),[3] δ = 1·40, 1·31; Δ = 1·16, 1·34. [c] Values taken from ref. 5.

Compounds with One Sn–S *Bond*.—The Mössbauer parameters for some tributyltin and triphenyltin compounds in the solid state and in solution in pyridine are given in Table 3. The quadrupole splittings of simple tetrahedral R_3SnX compounds have been shown[15] by calculation and experiment to be lower than those of compounds containing planar R_3Sn groups in a trigonal bipyramidal environment as found, for example, in associated R_3SnX compounds (I)[16] or in pyridine adducts (II).[17] Hence a compound such as (31) which is considered to have the five-co-ordinate structure (I) in the solid state[5] is expected, and is found, to have similar values of the quadrupole splitting in the solid state and in frozen pyridine solution. Compounds (22), (24), (26), and (27) have structures approximating to tetrahedra in the solid state and the higher values of Δ(pyridine) over Δ(solid) of 0·5—1 mm s^{-1} probably indicate interaction with pyridine to give unstable structures approximating to (II). The smaller increases in the quadrupole splittings of compounds (23) and (29) when the pyridine solution measurements are compared with the solid-state values may reflect reduced Lewis acidity in these compounds. The remaining compounds in Table 3, *i.e.* (25), (28), and (30), have potential chelating groups attached to tin and all showed increased values of the quadrupole splittings when solutions in pyridine were examined. These increases indicate that the R_3Sn groups are more planar in frozen pyridine than in the pure solid state but the structural implications of this are uncertain.



(I)



(II)

Finally, the lowering of the electron density at tin caused by replacing butyl by phenyl groups is shown by the generally lower values of the isomer shifts of the triphenyltin compounds compared with the tributyltin compounds.

EXPERIMENTAL

Details of the Mössbauer spectrometer have been described elsewhere.[18] Measurements were made with the samples at 78 K, the spectra were calibrated using β-tin and tin(IV) oxide, the separation being 2·56 mm s^{-1}. The error associated with the isomer shift and quadrupole splitting measurements does not exceed ±0·05 mm s^{-1}. The Mössbauer results were computed on the University of London Atlas Computer using a program kindly supplied by Dr. T. C. Gibb[19] which was modified to suit our requirements. The units for the isomer shifts (δ), quadrupole splittings (Δ), and line widths (Γ) quoted in the Tables are mm s^{-1}. Isomer shifts refer to tin (IV) oxide.

Mössbauer measurements in a magnetic field of 60 kG were carried out on compounds (6) and (11) with the specimens at 4 K by the P.C.M.U. (Harwell).

The following compounds were made by published procedures: bis(dithiolato)tin compounds (1)—(5)[7] and their adducts (6)—(20),[10] $(PhS)_4Sn$, 2,2′-bipyridyl,[20] phenylthiolatotributyltin,[21] and phenylthiolatotriphenyltin.[22]

Preparation of Thiolatotin Compounds.—*2-Aminophenylthiolatotributyltin*. Tributyltin oxide (1·45 g, 0·0024 mol) was suspended in dry benzene (50 ml) and 2-aminothiophenol (0·60 g, 0·005 mol) was added to it. The mixture was stirred for 1 h at room temperature and the water formed was removed azeotropically by distillation of the benzene. Distillation of the remaining oil gave the *product* (1·40 g, 70%) b.p. 140—145° at 1 mmHg (Found: C, 52·0; H, 7·5; S, 7·9; Sn, 29·0. $C_{18}H_{33}NSSn$ requires C, 52·3; H, 8·0; S, 7·8; Sn, 28·6%).

Similar procedures were used to prepare the following compounds. *2-Aminophenylthiolatotriphenyltin*, m.p. 86—90° (Found: C, 61·0; H, 4·4; S, 6·8; Sn, 25·1. $C_{24}H_{21}NSSn$ requires C, 60·8; H, 4·5; S, 6·8; Sn, 25·0%). *Ethane-1,2-dithiolatobis(tributyltin)*, b.p. 178—179° at 1·5 mmHg (Found: C, 47·2; H, 8·8; Sn, 34·6. $C_{26}H_{58}S_2Sn_2$ requires C, 46·3; H, 8·7; Sn, 35·2%). *Ethane-1,2-dithiolatobis(triphenyltin)*, m.p. 128—129·5° (Found: C, 57·1; H, 5·3; Sn, 29·5. $C_{38}H_{34}S_2Sn_2$ requires C, 57·6; H, 4·3; Sn, 30·0%).

Preparation of Thioacetates.—*Triphenyltin thioacetate*. A mixture of triphenyltin oxide (3·6 g, 0·005 mol), thioacetic acid (0·91 g, 0·012 mol), and dry toluene (150 ml) was stirred (2 h) at room temperature. The water pro-

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[16] See ref. 4, p. 201.

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[19] B. J. Duke and T. C. Gibb, *J. Chem. Soc.* (*A*), 1967, 1478.

[20] R. C. Poller and J. A. Spillman, *J. Organometallic Chem.*, 1966, **6**, 668.

[21] M. E. Peach, *Canad. J. Chem.*, 1968, **46**, 211.

[22] D. Blake, G. E. Coates, and J. M. Tate, *J. Chem. Soc.*, 1961, 618.

duced and most of the toluene were removed by distillation; the concentrated solution were filtered and the remaining solvent removed under reduced pressure. The resulting oil slowly solidified and was crystallised from benzene–light petroleum (b.p. 80—100°) to give colourless *crystals* (2·9 g, 68%) m.p. 92—93° (Found: C, 56·8; H, 4·5; S, 7·8; Sn, 28·2. $C_{20}H_{18}OSSn$ requires C, 56·5; H, 4·3; S, 9·5; Sn, 27·9%).

The same procedure was used to prepare *tributyltin thioacetate*, b.p. 166—168° at 2 mmHg (Found: C, 46·1; H, 8·3; S, 9·0; Sn, 32·8. $C_{14}H_{30}OSSn$ requires C, 46·0; H, 8·3; S, 8·8; Sn, 32·5%).

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